Title
SEMICLASSICAL THEORIES and QUANTUM HARDWALL CALCULATION OF ATOM SURFACE SCATTERING

Permalink
https://escholarship.org/uc/item/3fk5n8bm

Author
Masel, R.I.

Publication Date
1975-10-01
Published in the Journal of Vacuum Science and Technology, Vol. 13, No. 1, 355 - 359 (January/February 1976)

SEMICLASSICAL THEORIES AND QUANTUM HARDWALL CALCULATION OF ATOM SURFACE SCATTERING

R. I. Masel, R. P. Merrill, and W. H. Miller

October 1975

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Semiclassical theories and quantum hardwall calculation of atom surface scattering*

R. I. Masel and R. P. Merrill

Department of Chemical Engineering, University of California, Berkeley, California 94720

W. H. Miller

Department of Chemistry and IMRD, University of California, Berkeley, California 94720

(Received 25 August 1975; in final form 28 October 1975)

A semiclassical formalism for atom and electron scattering from solid surfaces is presented and compared to exact quantum calculations for scattering from a sinusoidal hardwall and to experimental scattering distributions for thermal helium and neon beams scattered from W〈112〉. The helium results are well represented by elastic calculations, but large inelastic effects are evident in the neon scattering. The semiclassical calculations for the hardwall are in agreement with the exact quantum results to within a few percent. Qualitatively, either a specularly dominated distribution or a rainbow pattern is predicted, depending on the \( k \) vector and the amplitude of the surface periodicity. A preliminary attempt to apply this formalism to low-energy electron scattering from Ni(100) is also presented. The results, while not in exact agreement with more conventional dynamic LEED calculations, do reproduce absolute peak positions to within 7 V.


INTRODUCTION

In recent years there has been a great deal of experimental and theoretical interest in the scattering of well collimated beams of rare gases and simple molecules from single crystal faces.1 In these experiments an atomic or molecular beam is directed onto the test surface at a preselected angle and one measures the angular distribution of scattered particles. Typical results for scattering of thermal beams from highly structured surfaces [in this case the (110) direction of W〈112〉], are shown in Fig. 1 for He (Ref. 2) and Ne (Ref. 3).

The He diffracts, exhibiting a strong specular peak and two less intense secondary peaks, which can be shown to correspond to first order diffraction beams. By contrast, neon scattering has a form referred to as “rainbow” scattering. It is much broader with less structure. The intensity maxima which are observed do not correspond to any particular diffraction condition. The angular positions of the most prominent maxima, one forward-scattered and one backscattered, are termed the “rainbow angles.”

Potentially the elastic part of these scattering profiles will yield information about the structure (i.e., morphology) of the surface potential while the inelastic part of the scattering profiles can yield information about surface phonons, gas-solid collision dynamics, and adsorption mechanisms. Here, the focus will be on the elastic part. The results of a dynamic, semiclassical theory4 of the scattering processes will be presented and compared to quantum hardwall calculations5 and some experimental data from W〈112〉. The purpose of these dynamical calculations is to identify the nature of the structural information which can be recovered from the elastic scattering.

SEMICLASSICAL LIMIT

The semiclassical theories are best presented via the Feynmann path integral6:

\[
\mathcal{S}(r_2,r_1,t_1,t_0) = \int_{\text{all possible paths from } r_1 \text{ to } r_2} \mathcal{D}[r(t)] \left[ \frac{\text{probability amplitude for the path } r(t)}{r(t)} \right], \tag{1}
\]

Fig. 1. A comparison of helium and neon scattering patterns in the (110) direction of W〈112〉. Data is from White.4
where $\mathcal{K}$ is the propagator kernel. Equation (1) represents a system by examining all the possible ways it can evolve and then assigning a probability amplitude to each path. The integral simply sums these probability-weighted paths. Work in gas-phase scattering\(^9\) has shown that it is a reasonable approximation to consider only those paths that satisfy classical mechanics. If this approximation is made then it is easy to show\(^4\) that the scattering amplitude $S(\theta)$ is given by

$$S(\theta) = [(\text{classical part})$$

$$\times (\text{structure factor for intracellular interference})$$

$$+ (\text{tunneling correlations})]$$

$$\times (\text{diffraction conditions}). \quad (2)$$

In Fig. 2 the classical part is plotted as a dotted line. It is rainbow-like, with two sharp infinities and a broad minimum. The infinities are caused by the many trajectories which contribute to scattering at these maximum allowed scattering angles (i.e., there is a maximum in the classical deflection function). This leads to infinities in a differential intensity at the rainbow angles. Semiclassical theory attenuates and broadens these infinities and produces supernumerary rainbows, i.e., periodic maxima within the rainbow angles. The interference which gives rise to these maxima occurs because two stationary phase trajectories add amplitudes for each scattering angle. It is analogous to the interference caused by scattering from different atoms within a unit cell in x-ray diffraction. The product of this “structure factor” and the classical part added to the tunneling corrections are also shown (solid line) in Fig. 2. When the diffraction conditions are imposed, the results are as shown in Fig. 3. If the wavelength of the incident particles is large (dark lines in Fig. 3), then most of the intensity will be in the specular peak, and only a small amount of intensity will be in the diffraction peaks. Lowering the wavelength (dashed lines) moves in the diffraction peaks and raises their relative intensity, producing a rainbow-like pattern. A similar effect can be seen if one changes the amplitude of the surface periodicity. Small amplitudes (smooth surfaces) result in rainbow angles close to the specular, which attenuate the diffracted beams strongly. Large amplitudes result in rainbow angles far from the specular, and the entire rainbow envelope modulates the intensities of the diffracted beams.

Qualitatively then, both types of scattering patterns normally observed (see Fig. 1) are recovered from the semiclassical calculations. A quantitative comparison is shown in Fig. 4. These are elastic semiclassical calculations of thermal (300 K) helium scattering from a modified Lennard-Jones 3-9 potential,\(^8\) and are compared to data of Stoll et al.\(^2\) for helium scattering from W(112). The results have been averaged over the experimental beam aperture. Relative intensities and peak positions are predicted to within experimental accuracy. Absolute peak intensities and peak widths are not predicted accurately, but it is expected that much of the difference would be eliminated by including in the calculations a Debye–Waller analysis with peak broadening.\(^2,8\)

A comparison with an experimental neon scattering pattern is shown in Fig. 5. Both the semiclassical calculations and the data show rainbow-like patterns, but there is little quantitative agreement. Inelastic effects have been ignored in the model, and neon scattering from tungsten is believed to involve strong inelastic effects.\(^9\)
QUANTUM HARDWALL CALCULATIONS

Since the semiclassical methods are approximate, it would be helpful to determine the magnitude of the errors associated with the formalism and to clarify as much as possible the physics implied by these techniques. While the coupled channel calculations of Wolken and Tschuda represent the exact quantum result for elastic scattering, the calculations are lengthy and make direct comparison with the semiclassical calculations over a broad range of system parameters impractical. It is worth noting, however, that Doll, using semiclassical techniques, has achieved close agreement with the Wolken results.

The coupled-channel calculations have been carried out for realistic potentials (i.e., Morse and Lennard-Jones). Simpler potentials can be treated by methods requiring less calculational labor. One such potential is a sinusoidal hardwall. This is a particularly interesting case for comparison with the semiclassical calculations because the impulse potential of the hardwall represents a "worse case" for semiclassical theory, and more physically realistic potentials should be represented even more accurately than the hardwall.

The formalism for the solution to the hardwall is based on the Lippmann–Schwinger equation:

$$\psi(r) = \phi_i(r) + \int dr_0 G^+(r,r_0) V \psi(r_0),$$

where $$\psi$$ is the wave function, $$\phi_i$$ is the incident wave, $$V$$ is the potential, and $$G^+$$ is the outward-going free-particle Greens' function. For a hardwall, the potential goes to infinity when $$z$$, the distance coordinate perpendicular to the surface, is less than the surface contour, $$D(x_0)$$. Equation (3) becomes

$$\psi(r) = \phi_i(r) + \int dr_0 G^+(r,r_0) \delta(z_0 - D(x_0)) f(x_0),$$

where $$f(x_0)$$ is yet to be determined.

For a sinusoidal surface it can be shown that the wave function above the surface is given by

$$\psi(r) = \exp(-ik \cdot r) + \sum_{l=-\infty}^{\infty} S_l \exp(ik_l \cdot r),$$

where

$$\exp(-ik \cdot r)$$ is the incident wave,

$$\exp(ik_l \cdot r)$$ are the diffraction beams,

with $$S_l$$ given by

$$S_l = \sum_{n=-\infty}^{\infty} C_n J_{l-n}(hak \cos \theta_l),$$

where $$\theta_l$$ is the angle of the $$l$$th order diffraction, $$a$$ is the lattice constant, $$h$$ is the amplitude of the surface periodicity, and the coefficient $$C_n$$ are determined by

$$\delta_{l,0} \cos \theta_l = \sum_{n=-\infty}^{\infty} C_n J_{n-l}(hak \cos \theta_l).$$

These calculations can be done essentially exactly. Some of the results are shown in Fig. 6. With increasing $$k$$ vector, the scattering distribution changes from a specular to a rainbow pattern, in qualitative agreement with the semiclassical model previously discussed. Quantitatively, the calculations that have been done so far indicate excellent agreement (within ~2%) between the exact calculations and the semiclassical ones.

In summary, the procedure at present is to assume a potential and calculate a scattering pattern, and then iterate on the potential until reasonable agreement with the experimental data is obtained. This procedure, while useful, suffers from the fact that it is not precise enough to define a completely unique morphology for the scattering potential. Scattering patterns at a single energy are not very sensitive to small changes in the interaction potential. By analogy to LEED and x-ray, more precision should be obtainable by examining the effect of energy of the incident beam on the scattering distributions. This has not yet been accomplished experimentally, but it can be done easily with the theory. Figure 7 is a calculated specular intensity as a function of increasing $$k$$ vector for a relatively rough hardwall ($$k=0.1$$); but one where multiple scattering

![Fig. 6. Quantum hardwall calculations of scattering at various energies, $$h_0=0.02$$, $$\theta_1=0$$](image-url)
in the classical trajectories is negligible. The semiclassical (○, ○, and X) and exact quantum results (solid line) are almost identical.

In the semiclassical formulation Bragg-like maxima from a sinusoidal hardwall are spaced according to the reciprocal of the amplitude of the surface periodicity \( \hbar \),

\[
\frac{n\hbar}{2\pi} = \frac{1}{2} \frac{1}{n+\frac{1}{2}} + \frac{(-1)^{l+1}}{4},
\]

where \( \hbar \) is the \( k \) vector for a peak maximum. The surface is nearly kinematic, but the specular peaks \( (l=0) \) are shifted by an almost constant amount \( (\pi/8\hbar) \) in \( k \) space. An empirical “inner-potential” could be used to shift the high energy peaks to their kinematic positions, but this procedure fails at lower energies because the shift is constant in \( k \) space but not in \( E \) space. There is a slight additional shift evident at low energies which arises because the envelope of the Bragg maxima is decreasing very rapidly with energy. When this envelope is multiplied by the periodic portion of the scattering intensity, the peak maximum shifts downward in \( k \) space. For the case shown in Fig. 7 this shift is \( \sim -0.5\hbar a \) for the first of the Bragg maxima. This same effect is also responsible for a monotonic decrease in the peak intensities at high energies.

Equation (8) is derived from the semiclassical calculations and predicts the \( \pi/8\hbar a \) \( k \) shift for the specular beam. The shift arises from a factor, \( \sqrt{\hbar} \), which enters through the phase addition of two trajectories scattered from different regions of the potential.

**ON DYNAMICAL LEED CALCULATIONS**

The complex \( I-V \) spectrum for LEED results from the dynamical interference among scattered beams from an array of discrete scattering centers near the surface of a solid. The analogous spectrum for atom scattering from the hardwall (Fig. 7) is simple indeed by comparison, though similar spectra for more realistic potentials calculated via the semiclassical techniques are much more complex than Fig. 7.

From Fig. 7 it is clear that the semiclassical calculations do very well when \( \hbar a > 7 \) or 8. For electrons this corresponds to energies of 10–30 eV which is below the energies where reliable LEED data can normally be obtained experimentally and below the energies where most dynamical calculations have been attempted. It is also interesting to note that semiclassical calculations have been applied to electron scattering from gas-phase atoms. Above about 30 eV the experimental results are well represented.

These considerations suggest that dynamical LEED calculations may be possible using semiclassical techniques. The most lengthy portion of currently used calculations is determining the scattering within a single layer of atoms within the surface selvidge, and it is possible that semiclassical calculations can be applied to this portion of the problem. Of course the LEED scattering is far from elastic, yet most procedures represent the inelastic interactions by a constant optical potential. Such “potential scattering” can be handled within the semiclassical formalism.

One approach is to invert the phase shifts to a scattering pseudopotential, calculate deflection functions, and identify the pertinent stationary phase trajectories from the layer symmetry. These trajectories are then used to calculate the intralayer scattering. The sum over layers can be handled using current procedures.

Figure 8(a) shows an initial attempt at calculating a LEED \( I-V \) spectra using this procedure. The intensity of the specular beam is plotted, as a function of energy for scattering at normal incidence, from a stationary Ni(001) surface. This is a crude calculation in that only those trajectories that scatter once or start in the incident beam and scatter twice were included in the single-layer sum. The multilayer sum was done exactly using RFS perturbation theory.\(^\text{13}\) Five phase shifts were used.

In Fig. 8(b) are plotted the five phase-shift calculations of Kesmodal\(^\text{14}\) and in Fig. 8(c) are plotted the data of Anderson\(^\text{15}\) (at 300°K). Considering the limited multiple scattering which has been included in the semiclassical calculations, they have done remarkably well. All of the major peaks in the \( I-V \) spectrum appear in the calculations, although peak positions and relative peak intensities are not reproduced exactly. This is much better than one might have expected from such a simple calculation. At present the calculational procedures are being modified so that more of the intralayer multiple scattering can be included.

Considering the success of this relatively simple initial calculation, it would appear that semiclassical methods can be used to calculate LEED \( I-V \) spectra. Semiclassical methods have a twofold advantage over more conventional LEED calculations: first, they are computationally efficient; and second, they help to make the physics of the dominant features of the scattering more transparent. It may be the latter that will make the semiclassical methods the most useful. If, for example, key features of the \( I-V \) spectra can be...
FIG. 8. The intensity of the specular beam as a function of energy for low-energy electron diffraction at normal incidence from Ni(100), normal incidence calculation, (a), (b) are for an optical potential of 14+3.6i V and 5 Wakoh phase shifts: (a) semiclassical calculations, stationary lattice; (b) quantum calculations of Kesmodal,14 stationary lattice; (c) data of Anderson,15 T = 300 K.

identified with relatively simple scattering trajectories such as singly or doubly scattered paths, then it may be possible to use such features to deduce structural parameters without reproducing the complete experimental $I-V$ spectra. Likewise, it seems probable that delineation of the dominant physics in the diffraction experiment may lead to more efficient averaging procedures and more useful transform methods than those which have been suggested so far.

**CONCLUSION**

The semiclassical theories can be used successfully for atom surface scattering calculations. They are in nearly quantitative agreement with exact calculations from a sinusoidal hardwall potential and represent experimental flux distributions very well indeed for thermal beams. The possibility of using the methods for dynamical LEED calculations is being investigated and a preliminary calculation for Ni(100) suggests the approach is promising.

**ACKNOWLEDGMENT**

We acknowledge L. Kesmodal for providing us with unpublished calculations.

*This research has been sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under AFOSR Grant No. 72-2218 and by NSF Grant GP-34199X. Computations were carried out on a Dacraft 6024/4 minicomputer funded by NSF Grant GP-39317 and on a CDC 6400, funded by a special grant from the Univ. of California Computer Center. W.H.M. acknowledges support from a Camille and Henry Dreyfus Teacher-Scholar Grant.


R. E. White, M.S. thesis (University of California at Berkeley, 1974).


14 L. Kesmodal (personal communication); S. Y. Tong and L. Kesmodal, Phys. Rev. B 8, 3753 (1975).

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.